

Enhancement of Beryllium Detection Limits Using Optical Fluorescence Method

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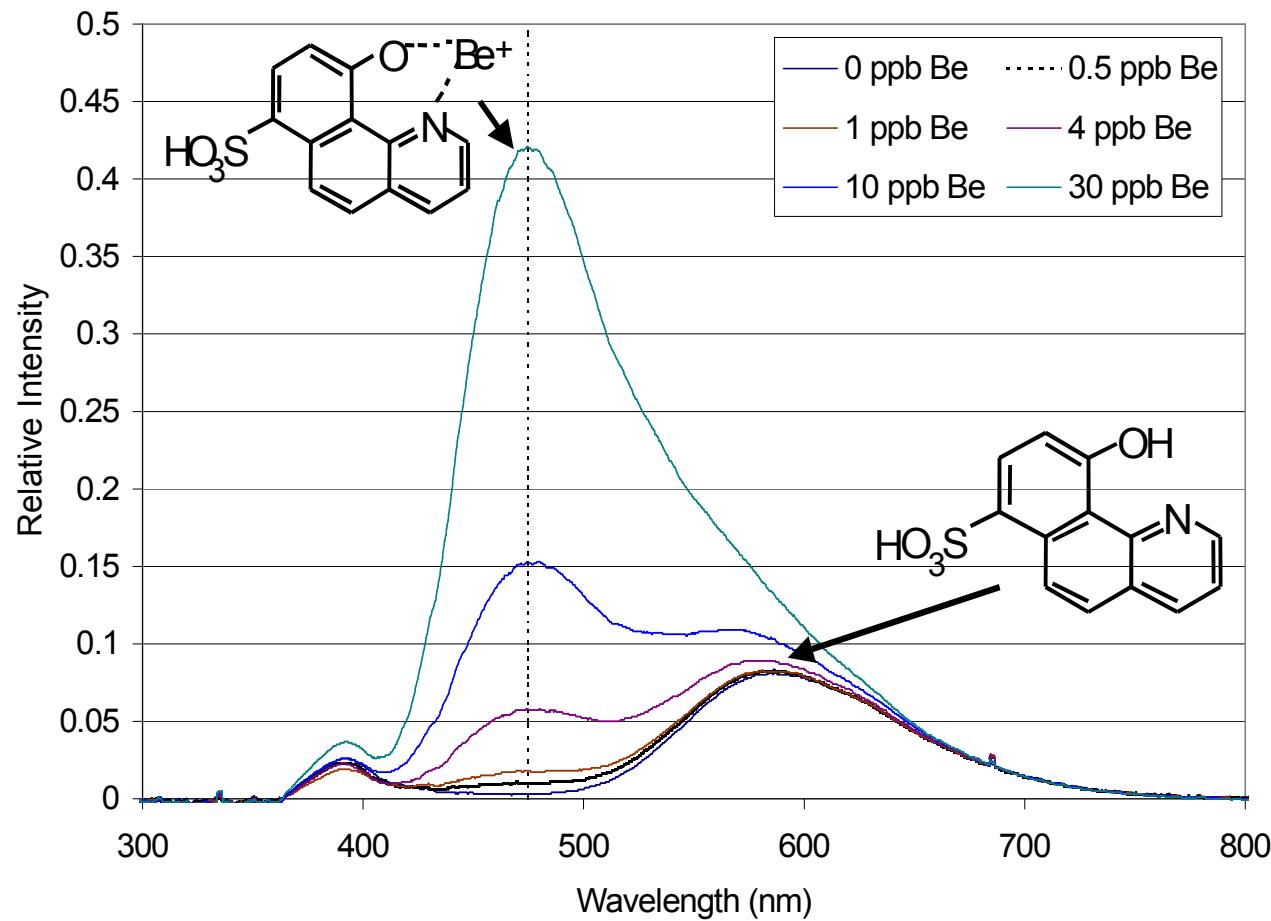
Optical Fluorescence Method for Beryllium Analysis

- Fluorescence system developed at Los Alamos National laboratory (LANL).
- Berylliant Inc licensed the technology from LANL.
- Commercial system developed and is available from Berylliant Inc as “BeFinder” system.
- Berylliant supplies both materials and equipment (www.berylliant.net).

Standard Methods and Accreditation Status

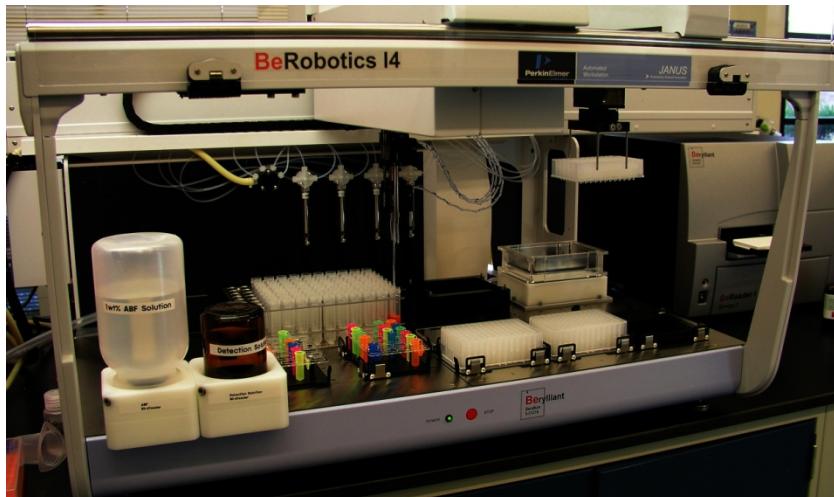
- Approved Methods
 - NIOSH 7704 (air)
 - NIOSH 9110 (wipes)
 - ASTM D7202 (wipes and air)
 - ASTM D7854 (bulk samples)
 - ASTM D7707 (Beryllium specific wipes)
- AIHA will accredit laboratories (including field operations) using this procedure.

Method Principles



HBQS (hydroxybenzoquinoline sulfonate) dye solution
is excited at 365 to 380nm and measured at 478nm

Simple Implementation



Automated high-throughput system



BeFinder Manual Fluorometer

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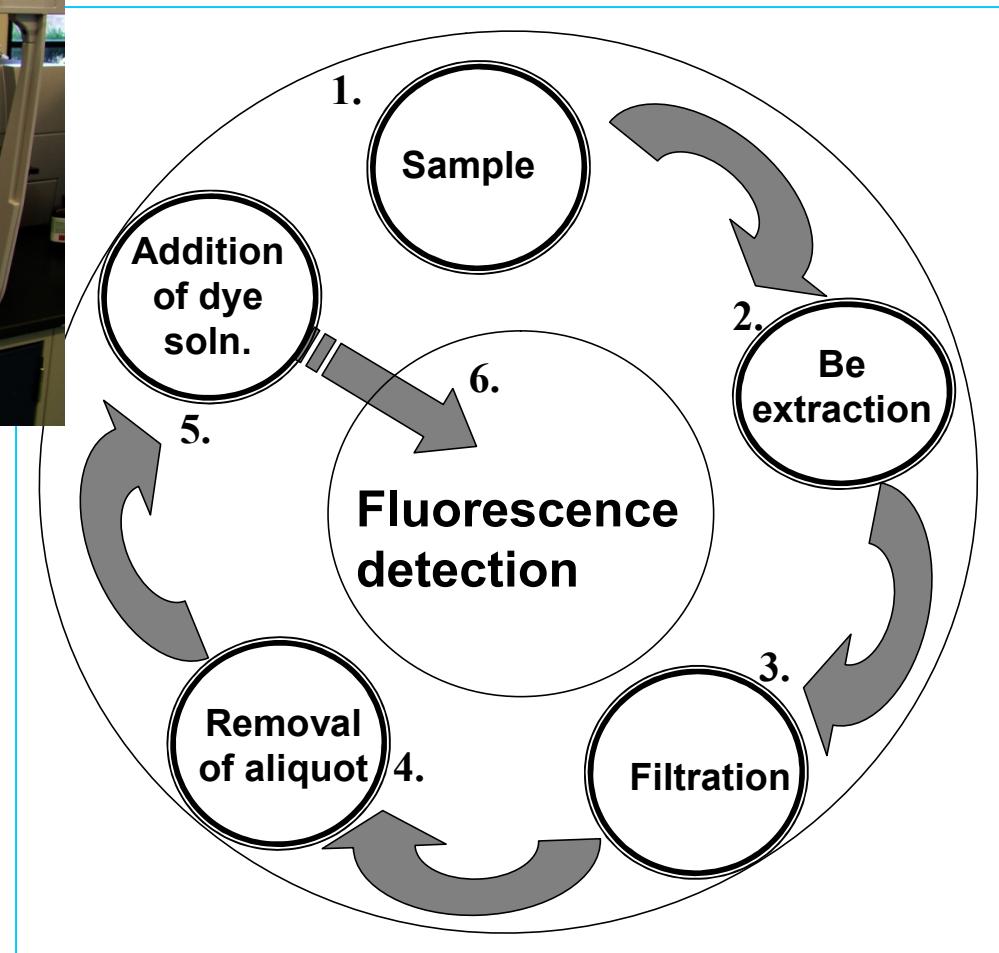
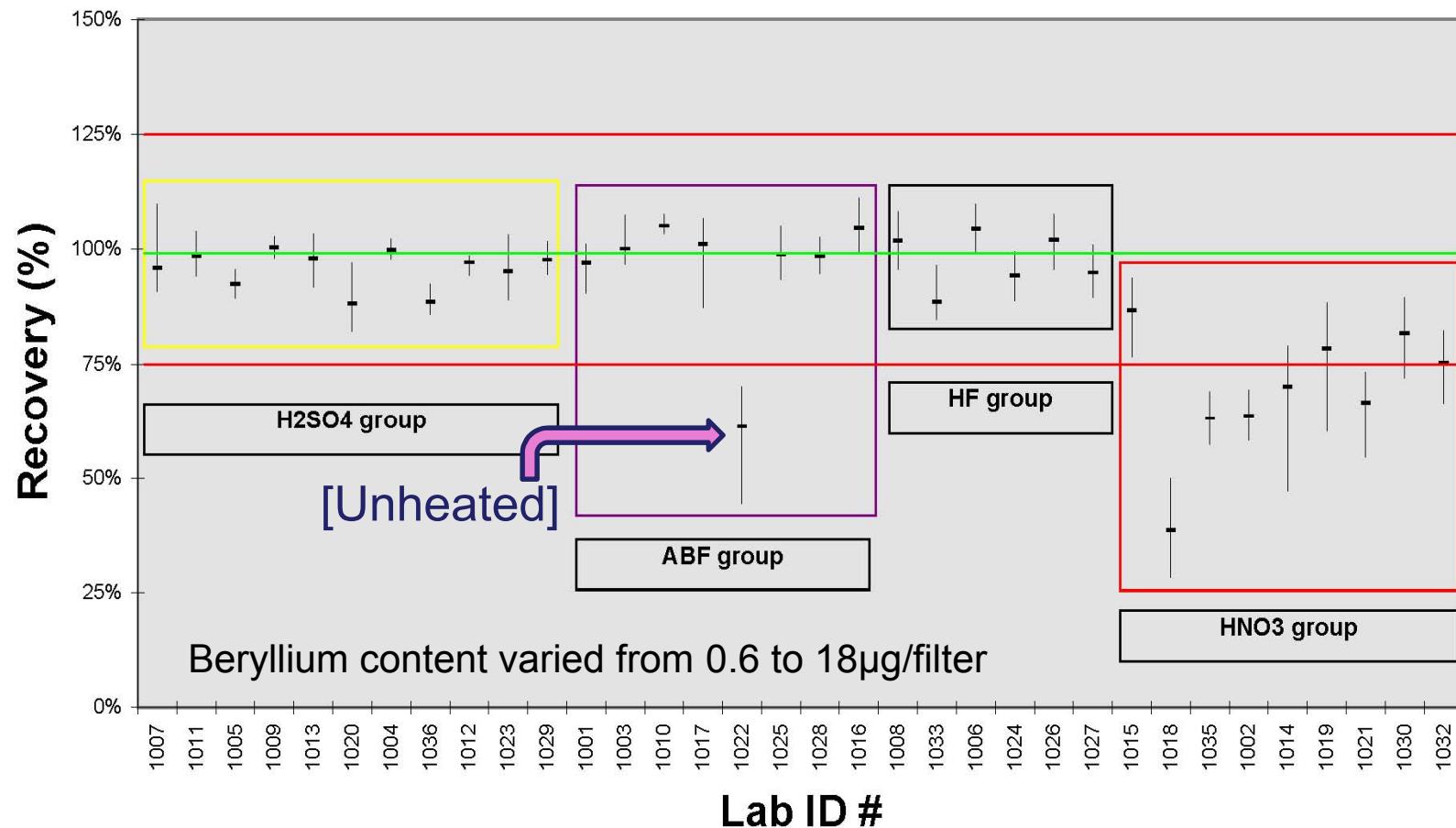


Table 5 Interlaboratory round-robin analysis results ($n = 9$) from MCE and Whatman 541 filters spiked with beryllium sulfate

Beryllium level/ μg Be sample $^{-1}$	Reported average \pm std. dev./ μg Be sample $^{-1}$	Inter-laboratory RSD ^a (%)	Estimated bias
MCE filters			
0.050	0.052 \pm 0.0034	6.5	0.040
0.10	0.10 \pm 0.0048	4.8	0.00
0.20	0.21 \pm 0.018	8.6	0.050
0.40	0.42 \pm 0.040	9.5	0.050
Whatman 541 filters			
0.050	0.053 \pm 0.0054	10.2	0.060
0.10	0.11 \pm 0.011	10.0	0.10
0.20	0.21 \pm 0.0094	4.5	0.050
0.40	0.41 \pm 0.025	6.1	0.025

^a (Relative standard deviation).

Dissolution methods: BeO-spiked filters interlaboratory study



Oatts, et.al., J. Environ. Monit., 2012, 14, 391

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Why do we Need to Lower the Detection Limits?

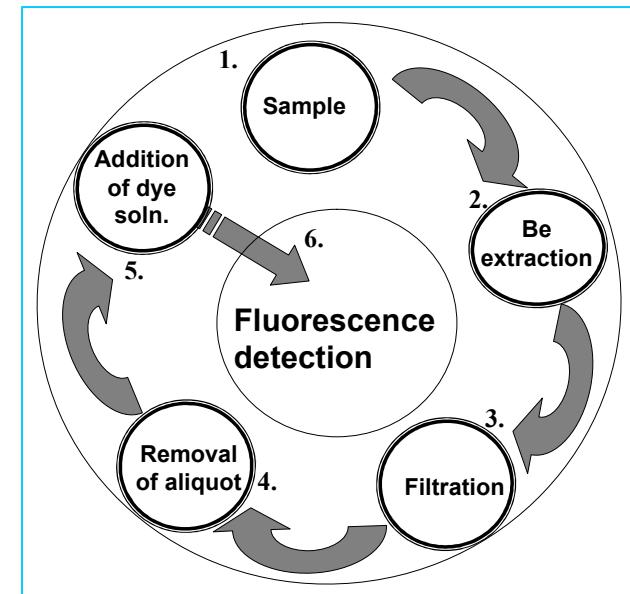
- At Present DOE requires compliance down to $0.2\mu\text{g}$ in air (eight hour time weighted average (TWA) on filters by passing one cubic meter of air).
- In case a facility needs to comply with $0.2\mu\text{g}$ TWA limit during short exposure (STEL of 15 minutes @ 2liter/min of air), then one would need to measure down to $0.006\mu\text{g}$.
- To measure $0.006\mu\text{g}$ reliably (0.06ppb at $20\times$ dilution), we prefer an LOD limit of **$0.0006\mu\text{g}$ (LOD of 0.006ppb)** or better.
- To determine if while using dilution ratio of $20\times$ (and using 1%ABF as dissolution solution) the detection limits can be pushed down .

Detection Limits* using Manual BeFinder Instrument

Dilution ratio (Sample solution vol: Dye Solution vol)	Detection Limit on sample wipe/filter, µg	Detection Limit in solution, ppb
5x (1:4)	0.0008	0.032
20x (1:19)	0.0015	0.015

0.006

* LOD established at 0.00075µg at 5X dilution using *Generation 1 instrument* (Turner Quantec), excitation at 365nm and emission at 460nm(K. Ashley et al. *Analytica Chimica Acta* 584 (2007) 281–286)



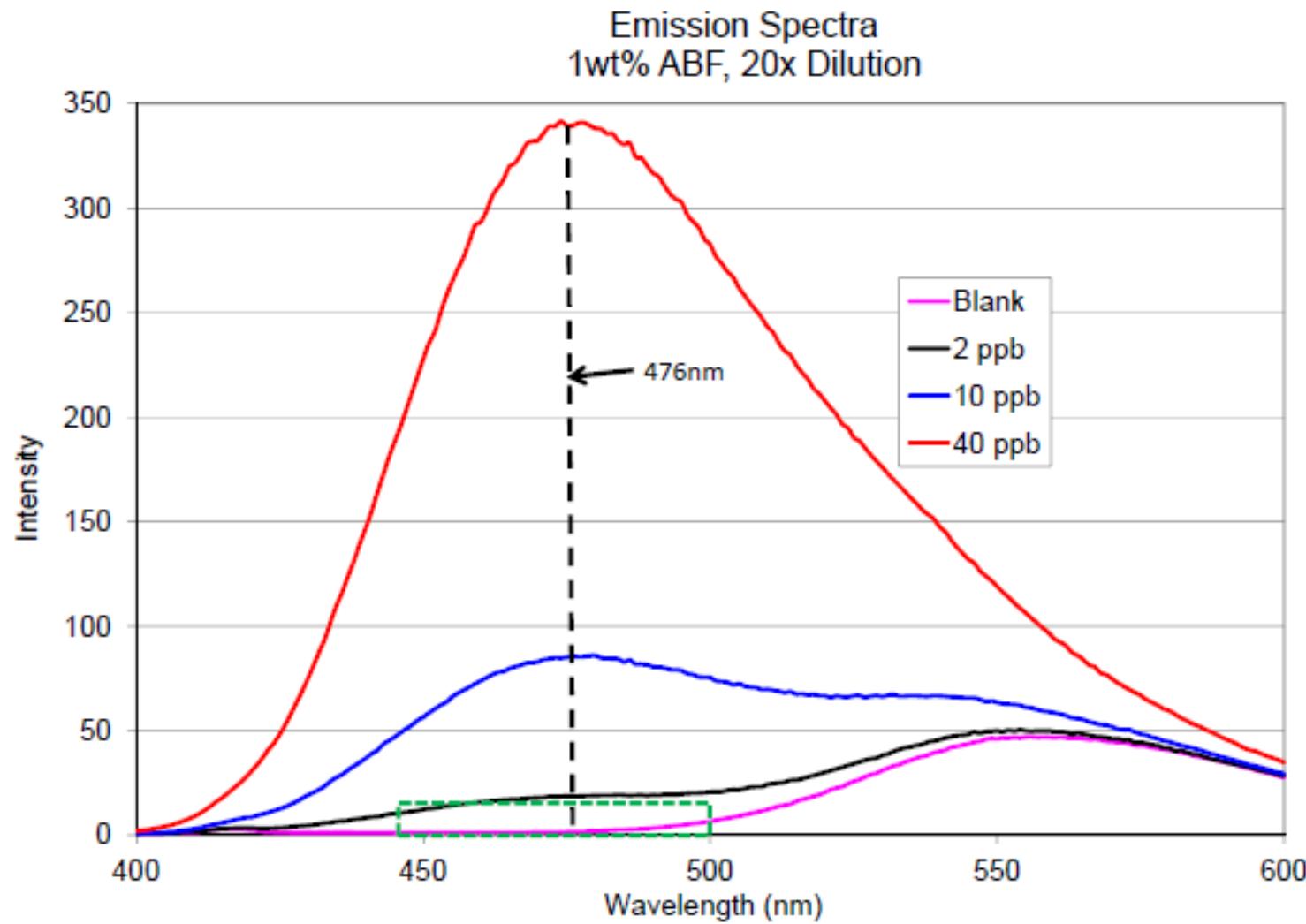
Study Parameters

- Adapted to suit **BeFinder** manual system
 - Dissolution solution 1%ABF
 - Dilution ratio 20X (1.9ml of dye solution+0.1ml of sample in dissolution solution)
 - Excitation @365nm
 - Need to determine emission filter characteristics

The methodology can be used universally to optimize other parametric combinations

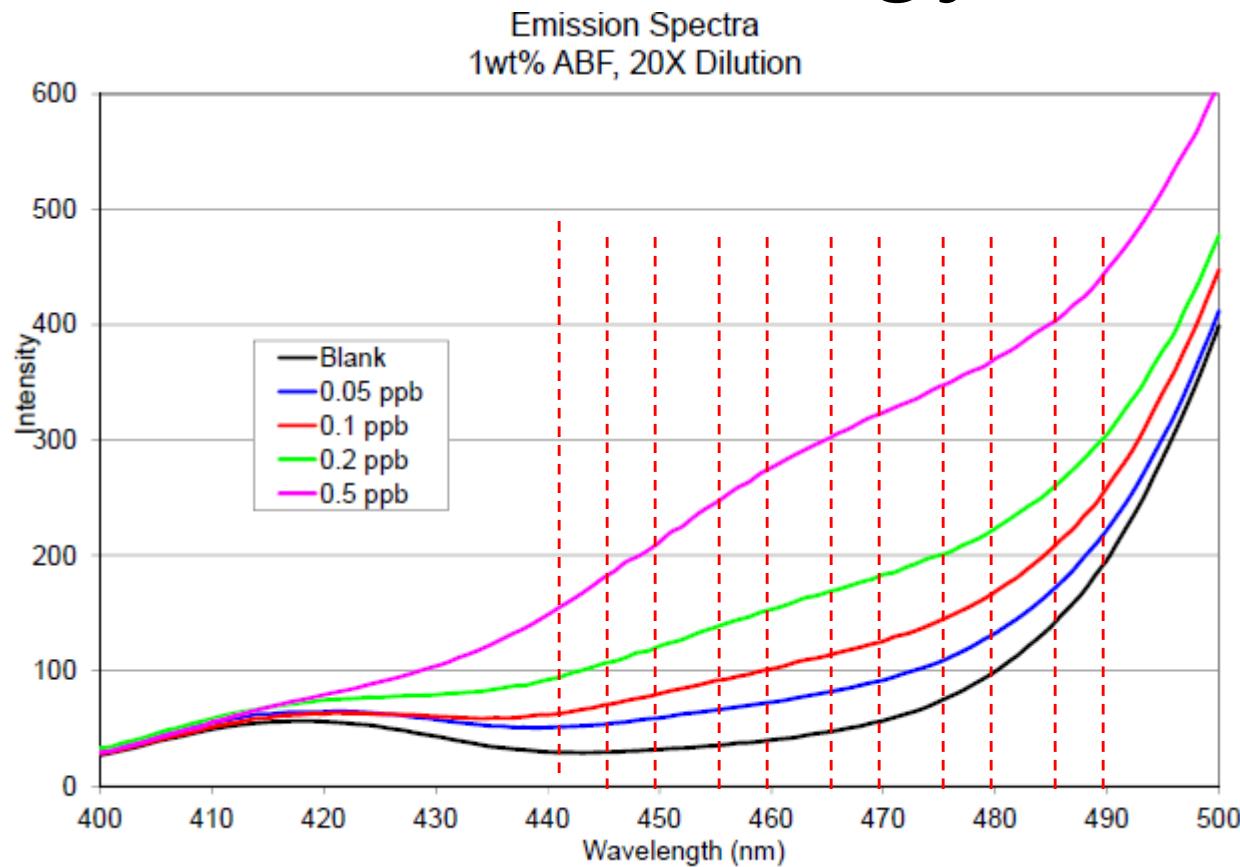


Methodology



October 12, 2012

Methodology

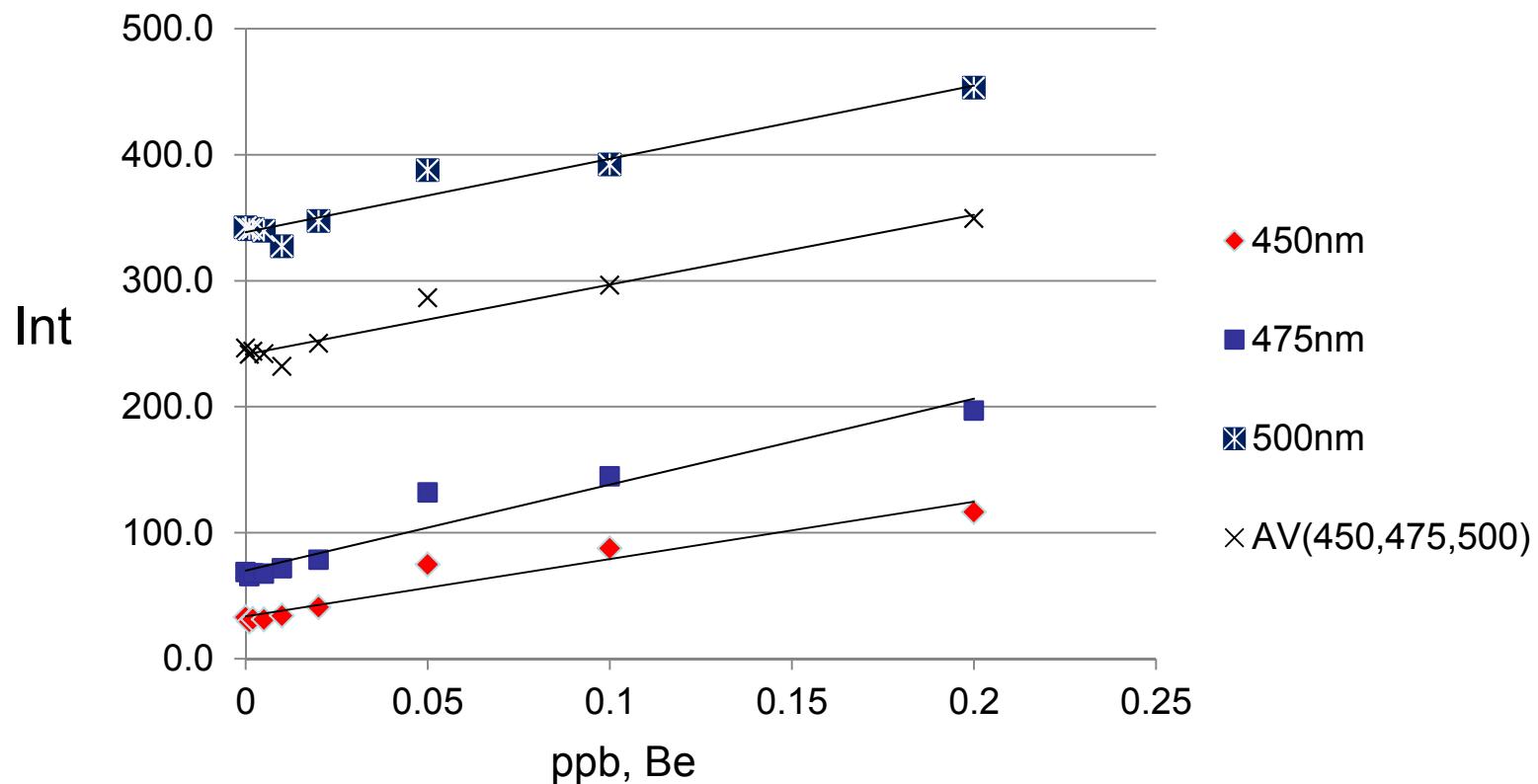


Increase light input to the detector which is correlated

Correlation at different Wavelengths

Std (ppb)															AV(450,475
Be)	445nm	450nm	455nm	460nm	465nm	470nm	475nm	480nm	485nm	490nm	495nm	500nm	505nm	510nm	,500)
0	30.6	32.9	36.2	40.3	46.7	55.5	68.8	91.2	124.2	173.2	246.2	342.4	472.5	638.1	246.6
0.001	28.0	29.6	32.9	36.8	42.6	51.0	65.5	87.5	121.2	169.7	243.1	340.9	471.4	630.0	241.7
0.002	30.1	31.6	34.5	39.2	45.0	54.2	67.7	89.1	122.2	171.8	243.3	341.3	469.5	632.6	244.0
0.005	28.6	31.1	34.2	38.6	44.8	53.6	67.6	88.9	123.2	171.7	243.6	339.6	470.1	627.3	242.0
0.01	31.5	34.2	37.7	43.0	49.2	58.9	72.0	93.5	125.2	169.7	237.7	327.4	446.7	589.8	232.0
0.02	37.7	40.9	44.3	49.9	56.0	65.4	78.6	100.6	133.4	180.1	252.1	347.3	474.8	631.4	250.3
0.05	67.8	74.8	83.9	93.1	104.1	116.1	131.9	155.5	188.1	233.4	299.2	387.9	506.0	652.5	286.4
0.1	78.9	87.6	96.5	106.9	118.3	130.0	144.9	166.8	197.8	240.1	306.3	392.2	507.5	657.3	296.6
0.2	100.4	116.4	133.9	149.4	165.1	179.0	197.0	219.4	252.5	296.2	363.4	453.2	577.6	734.6	349.3
R ² Value	0.915	0.932	0.941	0.944	0.943	0.942	0.942	0.938	0.940	0.939	0.946	0.942	0.914	0.821	0.959

Data Linearity and Pattern at different Wavelengths



Simulation of Various filters

Emission Spectra, Excitation at 365/20, Emission Slit Width of 3nm

Std (ppb Be)	AV(450,475,500)	Simulated filter effects		
		480/10 (475-485)	470/28 (456-484)	475/50 (450-500)
0	246.6	94.7	66.1	114.3
0.001	241.7	91.4	62.5	111.0
0.002	244.0	93.0	64.5	112.7
0.005	242.0	93.2	64.4	112.4
0.01	232.0	96.9	68.5	113.5
0.02	250.3	104.2	75.4	122.6
0.05	286.4	158.5	124.7	169.8
0.1	296.6	169.9	137.3	180.7
0.2	349.3	223.0	185.2	229.6
R² Value	0.959	0.9963	0.9996	0.9985

Results from Manual (**BeFinder**) Fluorometer

(excitation at 365nm, dilution ratio 20x, 1%ABF)

	Emission Filters, nm				
	465/30	480/10	470/28	475/50	
LOD*, ppb	0.015	0.002	0.003	0.003	
*Based on blanks	Desired LOD : 0.006 ppb or better				

Improvement in Data Quality						
Calibration Stds. ppb	40	10	2	0.5		
		10	2	0.5	0.1	
			2	0.5	0.1	0.5
ppb in sample	Readings, 480/10					
0.5	0.55	0.48	0.46			
0.2	0.31	0.23	0.24			
0.05	0.16	0.07	0.07			
0.02	0.12	0.01	0.01			
0.01	0.09	0	0.002			

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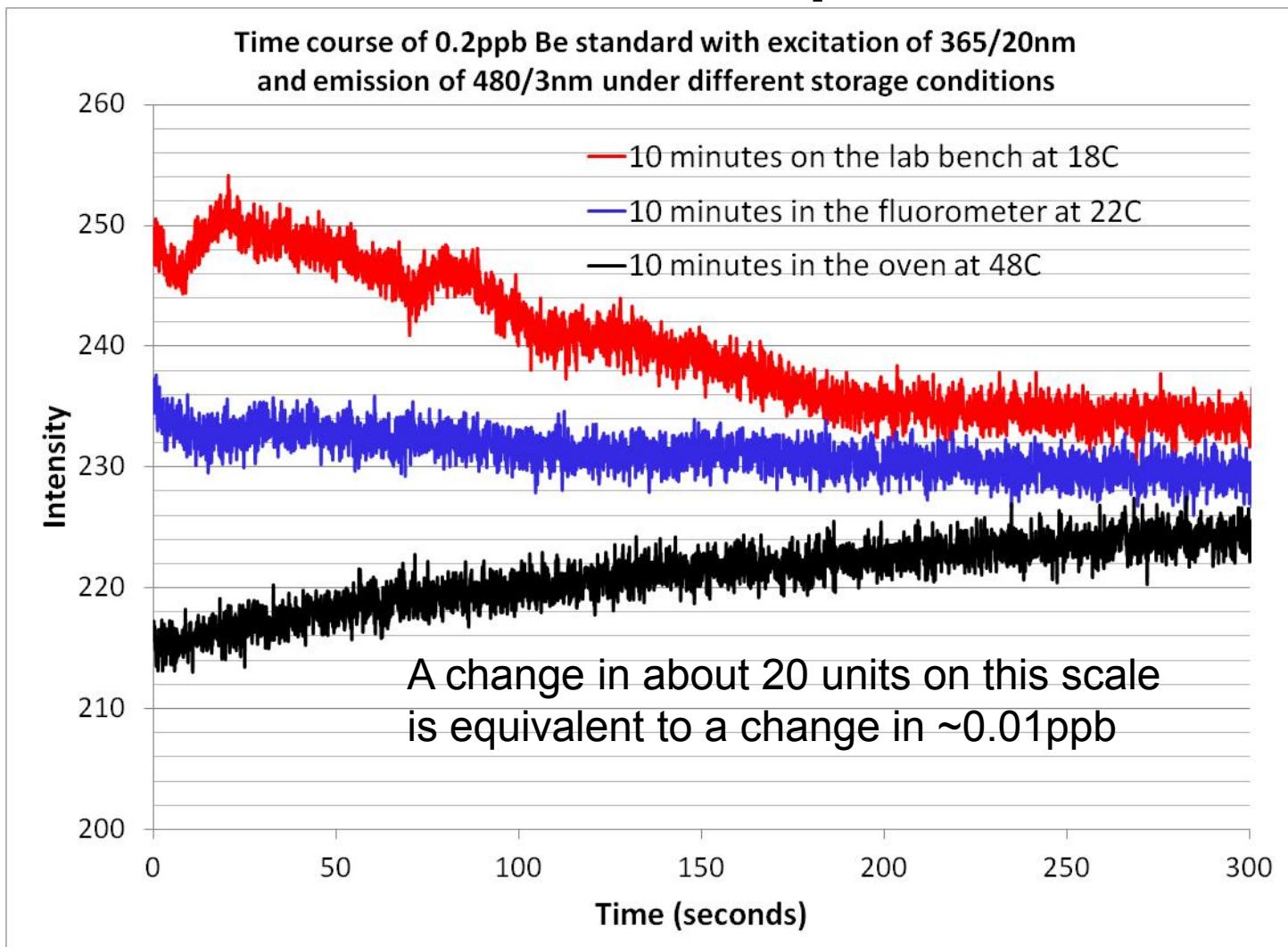


Testing of Data Quality

Calibration Standard (Max, ppb)	10	40
Correlation coeff	0.999999	0.999978
Readings for 0.05ppb		
Average (n=3)	0.068	0.120
Std deviation	0.003	0.003

Calibration Standard (Max, ppb)	10	40
Correlation coeff	0.999982	0.999996
Readings for 0.05ppb		
Average (n=3)	0.080	0.107
Std deviation	0.003	0.003

Effect of Temperature



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Current Conclusions

- Optimization of emission optical filter is important in increasing method sensitivity.
- For manual fluorometers (365nm excitation, 1%ABF and 20X dilution protocol) the following was determined:
 - Using a filter with transmission band at 480/10nm results in a LOD of 0.002ppb (0.2ng on media).
 - However, to improve data quality at values lower than 0.5ppb (50ng) recalibration should be done using more dilute standards ([redacted] 0.1, 0 ppb).
- It is important to control the temperature of the samples and the standards within 1°C or better.



Thank You

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